Multifunctional, Self-Healing Polyelectrolyte Gels for Long-Cycle-Life, High-Capacity Sulfur Cathodes in Li-S Batteries

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Project ID
bat320

Overview

Timeline

- Project start date – Oct. 2016
- Project end date – Sept. 2019
- Percent complete – 49%

Budget

- Total project funding
  - DOE share: $1.25 M
  - Contractor share: $138,888
- Funding received in FY 2017
  $416,667
- Funding for FY 2018
  $416,667

Barriers

- **Cost**: Reduce $/kWh of EV batteries using high-energy-density, low-cost Li-S chemistry
- **Performance**: Double the energy density of state-of-the-art Li-ion batteries using Li metal anode
- **Life**: Mitigate capacity loss mechanisms in Li-S cells for improved cycle life

Partners

- Project Lead: University of Washington
- Interactions/collaborations: Pacific Northwest National Lab

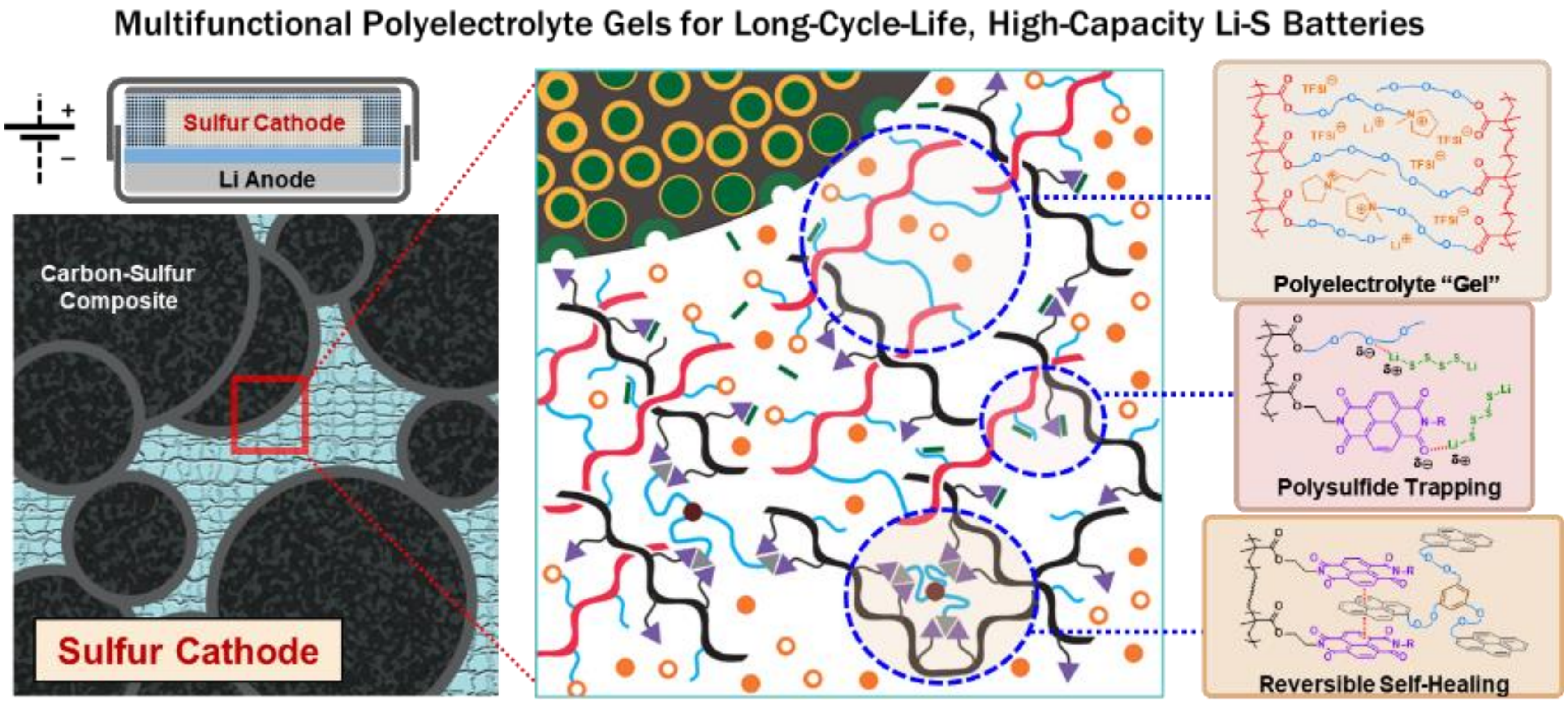
Relevance

- **Overall Objective:** Develop high-performance Li-S cells, based on self-healing and polysulfide-trapping polyelectrolyte gels containing solvate ionic liquid (SIL). The Li-S battery design will be capable of achieving gravimetric and volumetric energy densities of ≥800 Wh/kg and ≥1000 Wh/L, respectively.
- **Objectives this period**
  - Demonstrate gel electrolytes with ionic conductivity > 1mS/cm
  - Demonstrate polymers with tunable self-healing temperature (close to room temperature) and mechanical property
  - Design and demonstrate surface modification for mesoporous carbon to achieve improved capacity retention
- **Impact**
  - Li-S batteries has the potential of achieving the DOE goal of $100/kWh for battery pack usable energy

Milestones

Date	Milestone or Go/No-Go Decision	Status
June 2018	<u>Go/No-Go Decision</u> Selection of Gel Structure for Device Optimization	On track.
Dec 2018	<u>Milestone</u> Intermediate Cell Degradation Update	On track.
Mar 2019	<u>Milestone</u> Intermediate Cell Performance Update (Practical Cells)	On track.
Sep 2019	<u>Milestone</u> Optimized Cell Degradation Update	On track.

Approach/Strategy



Approach/Strategy

- **Carbon/Sulfur Composite**
  - Mesoporous carbon provides conductivity and physical containment of Li_2S_x
  - Platform to add targeted chemical functionality for performance enhancement
- **Solvate Ionic Liquid + Polyelectrolyte Gel**
  - IL electrolyte suppresses Li_2S_x dissolution and inhibits Li dendrite growth while providing conductivity similar to organic electrolytes
  - Gel creates mechanical toughness without sacrificing much conductivity
- **Trapping of Polysulfide Species**
  - Containment of Li_2S_x species *via* physical or chemical interaction eliminates redox shuttle effect and improves capacity retention
- **Self-Healing through Reversible Noncovalent Interactions**
  - Interaction of electron-rich (pyrene or “Py”) and electron-poor (naphthalene diimide or “NDI”) aromatic groups allows tunable, reversible binding
  - Introduction of reversible noncovalent binding induces self-healing, suppressing capacity loss due to mechanical degradation of cathode

Technical Accomplishments and Progress

Fabrication of High-Conductivity Ionogels

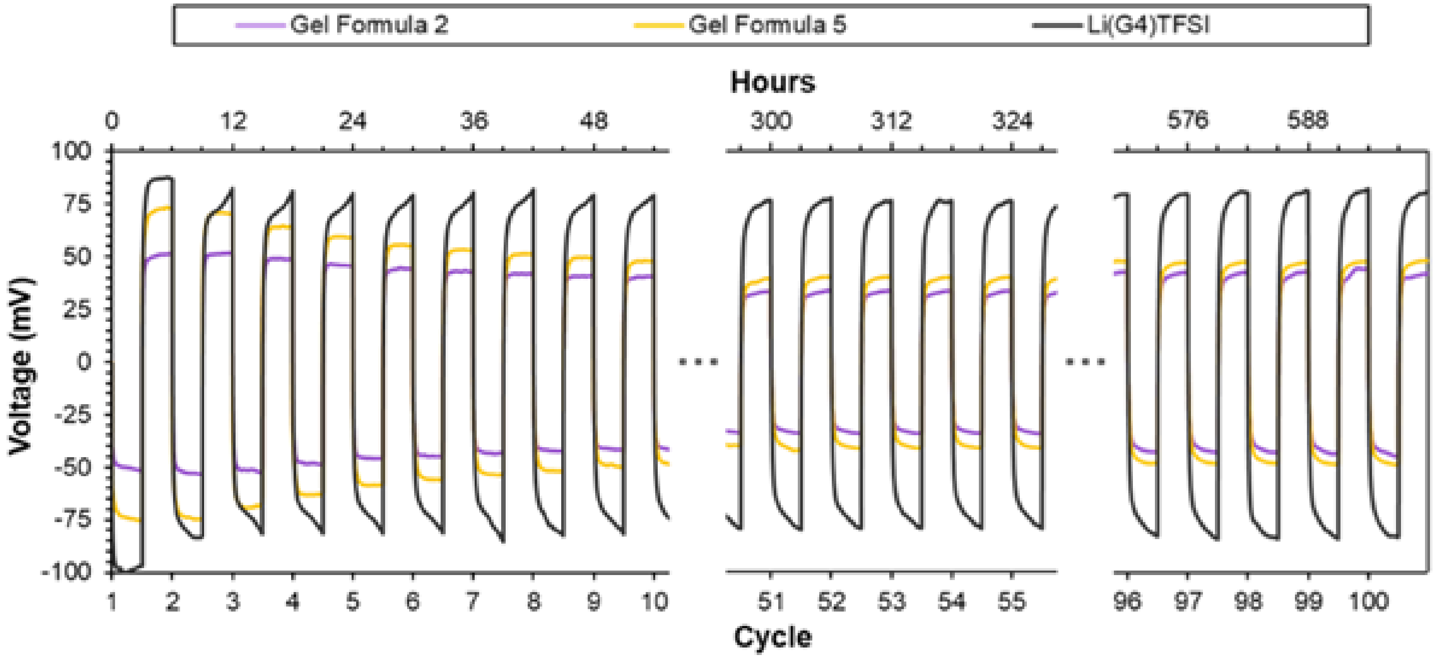
#	PEGDMA	PyrTFSIMA	TEGMA	Li(G4)TFSI	1,4-diox	σ (10^{-3} S/cm)
1	20%*	0%	0%	80%	0%	**0.73**
2	20%†	0%	0%	80%	0%	**1.05**
3	10%†	0%	10%	80%	0%	**0.92**
4	10%†	10%	0%	80%	0%	**1.07**
5	20%†	0%	0%	66.6%	13.3%	**2.15**

*M_n=750Da, †M_n=3500Da

- Reliable one-pot fabrication method produces thin ionogel films with remarkably high conductivity at 23° C
- Effect of both polymer and liquid composition on conductivity investigated to inform selection of formula for later cell optimization

Technical Accomplishments and Progress (cont.)

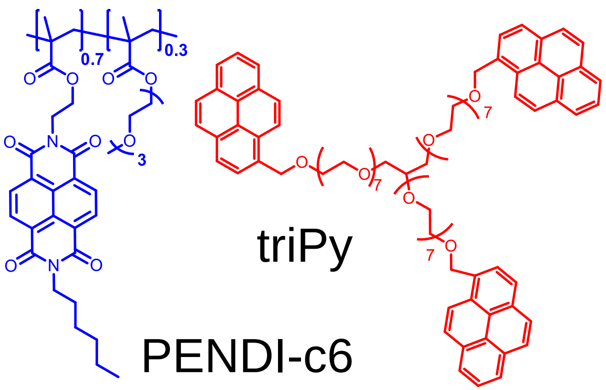
Ionogel Compatibility w/ Li Metal

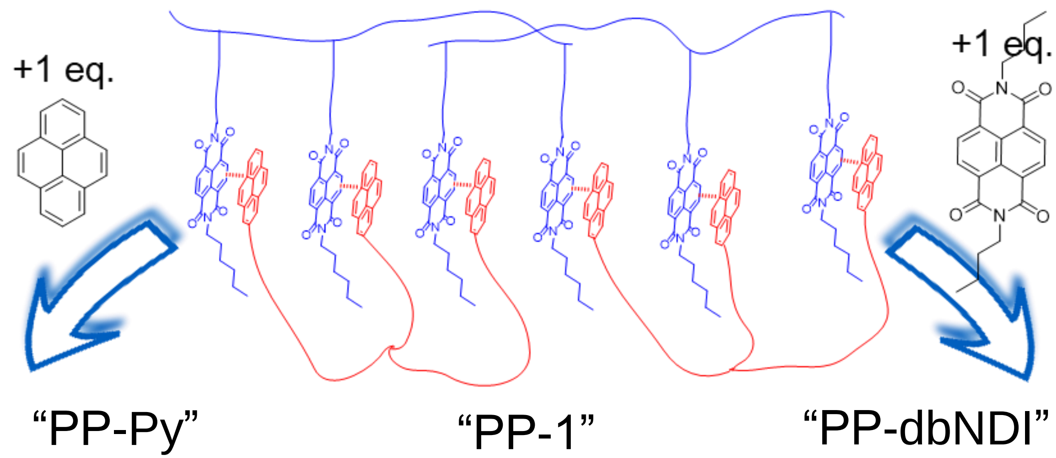


- Ionogel separators allow Li|Li symmetric cells to cycle stably ($\pm$0.1mA/cm^2) for over 600 hours at low overpotentials

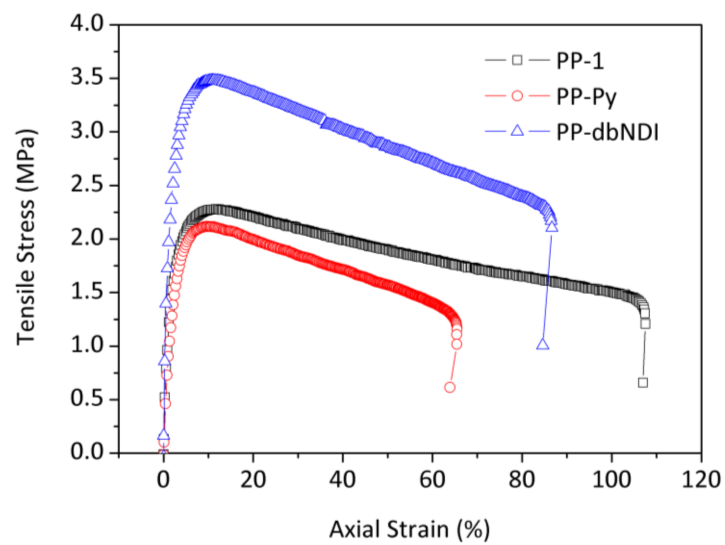
Technical Accomplishments and Progress (cont.)

Self-Healing Material Tunability



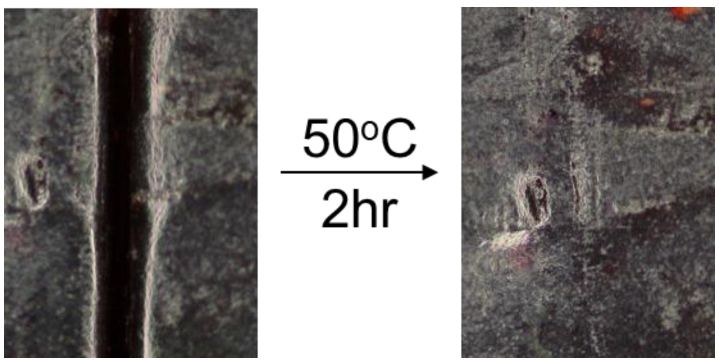


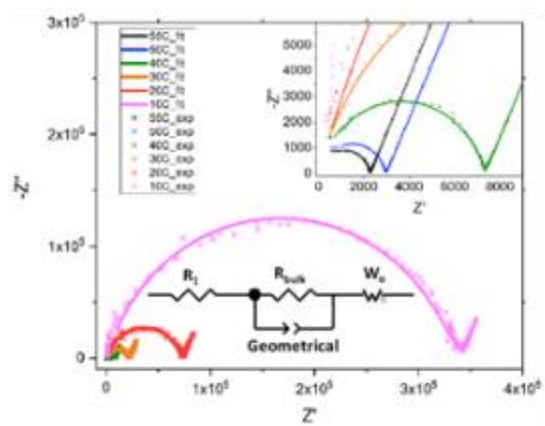
- NDI/Py interaction strength shown to depend on ratio of concentration
- Small-molecule dopants adjust ratios without altering polymer, allowing for tunable properties
- Elastic modulus: 63-250MPa

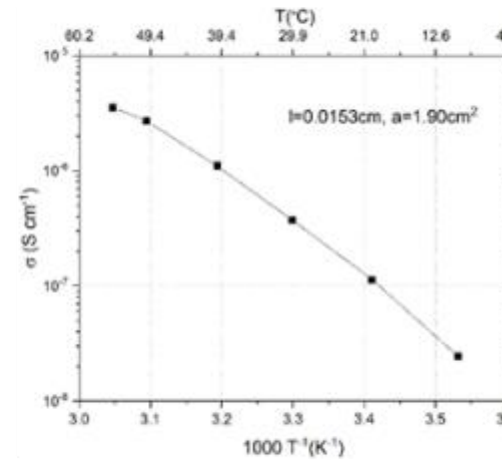


Technical Accomplishments and Progress (cont.)

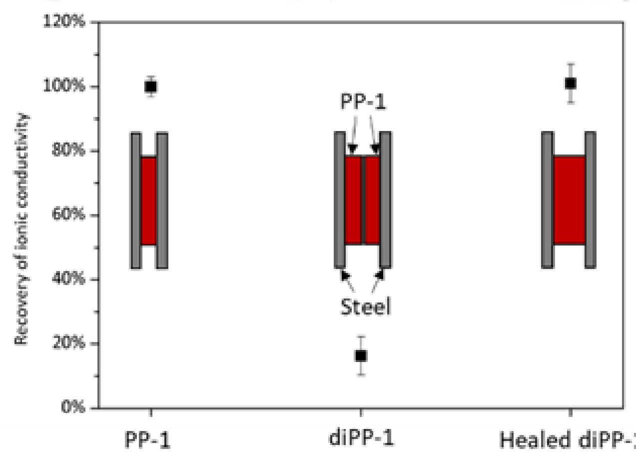
Influence of Temperature on PP Materials





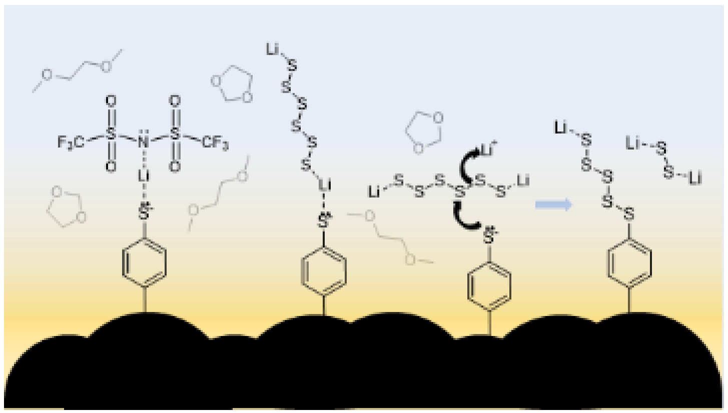


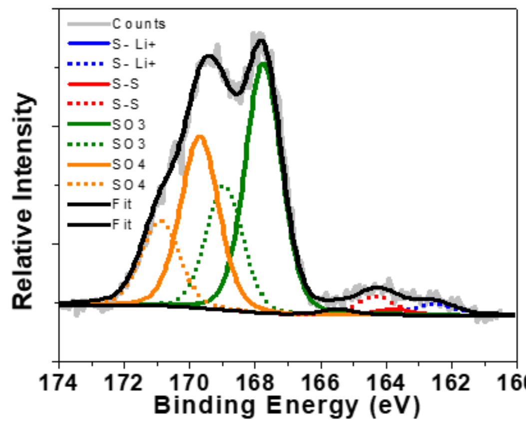
- Self-healing temperature tunable from 30-60° C
- Polymer acts as solid-state electrolyte w/ LiTFSI doping, recovers conductivity upon healing

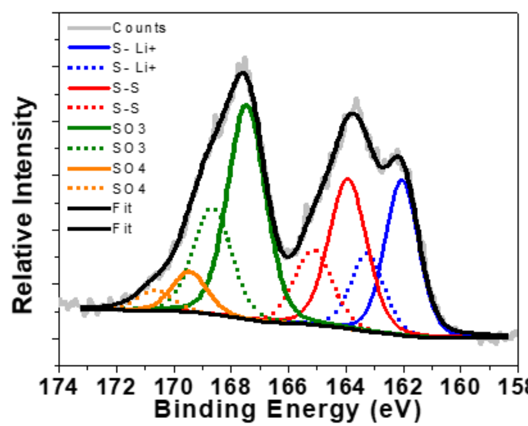


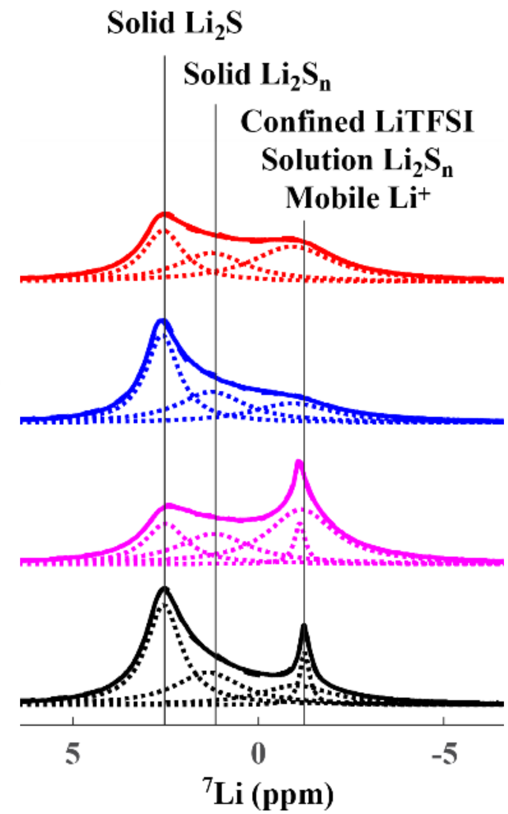
Technical Accomplishments and Progress (cont.)

Interaction of Thiol Surface with Li_2S_x, Electrolyte





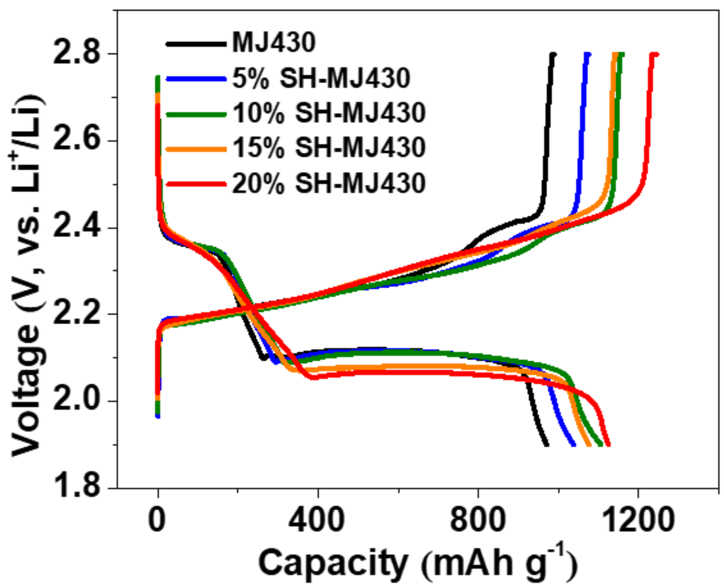


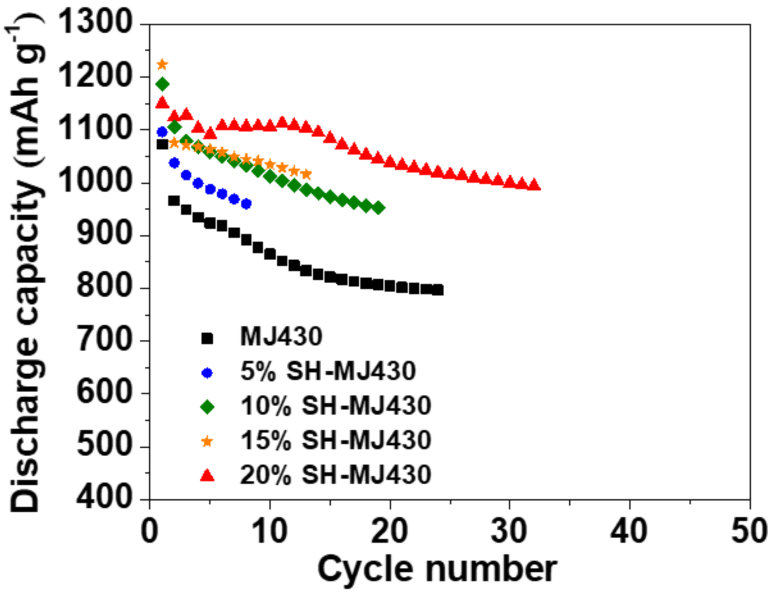


- Diazonium chemistry used to attach phenylthiol groups onto surface of mesoporous carbon host used for sulfur
- XPS of cycled cathodes shows covalent attachment of Li_2S_x
- ^{7}Li NMR shows increased electrolyte presence

Technical Accomplishments and Progress (cont.)

Enhanced Practical Cell Performance





- High-loading cathodes (4 mg_S/cm^2) fabricated with carbons of varying modifier concentration (as measured by weight loss during TGA)
- Discharge capacity and retention (C/10) increases with thiol loading, demonstrating beneficial effect of modified surface

Responses to Previous Year Reviewers' Comments

- This project was not reviewed at last year's AMR.

Collaboration and Coordination with Other Institutions

- The project is carried out by the Jen and Yang groups at the University of Washington
  - Jen: design and characterization of ionogel electrolytes, design and characterization of self-healing materials, surface modification of mesoporous carbon, electrochemical characterization of concept cells
  - Yang: carbon/sulfur composite characterization, surface modification of mesoporous carbon, design and electrochemical characterization of practical cells

- FY 18 Collaborator – Pacific Northwest National Laboratory
  - ^{7}Li NMR
  - Electron microscopy of carbon/sulfur composites

Remaining Challenges and Barriers

- We must continue to develop and optimize our procedure for curing ionogels *in-situ* around carbon/sulfur composite particles, effecting a gel cathode as initially proposed.
- The effect of our self-healing polymer system on a functioning sulfur cathode must be demonstrated using cell data.
- Quantitive demonstration of polysulfide trapping by gel functionality must be shown. We are in the final stages of developing a novel, generalized method to determine polysulfide concentration and average chain length in solutions.
- Sulfur/carbon composite design, including surface functionality, must be optimized appropriately for an ionogel electrolyte system.
- The predominant cell degradation mechanisms in gel cathode systems must be identified, and steps taken to mitigate them.

Proposed Future Research

- **Immediate Future**
  - Further characterize electrochemical and mechanical properties of our gel formulations
  - Characterize interpenetrated gels containing PP self-healing polymer
  - Quantify polysulfide trapping in our materials using novel fast determination method
  - Demonstrate Li-S cells with gel cathodes
  - Select set of gel components to continue optimizing around for best cell performance
- **Before March 2019**
  - Develop optimized ionogel electrolytes with very high conductivity and controllable polysulfide solubility/transport
  - Demonstrate significantly improved capacity retention and Coulombic efficiency in gel cathodes, compared to cathodes with traditional electrolyte systems
  - Demonstrate self-healing behavior in a functioning cell
  - Identify prominent performance degradation pathways in Li-S cells with gel cathodes using a combination of microscopy, spectroscopy, and electrochemical behavior

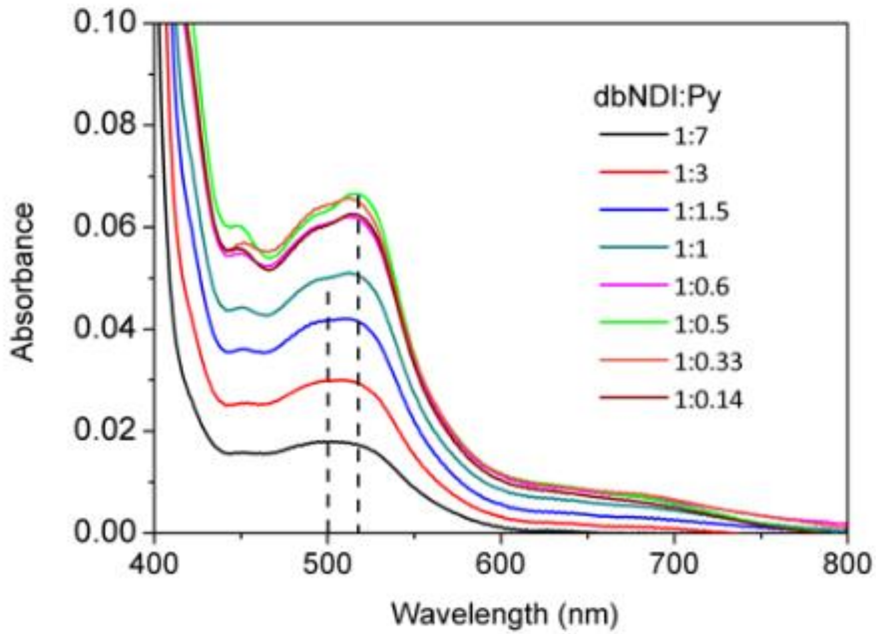
***Any proposed future work is subject to change based on funding levels*.**

Summary

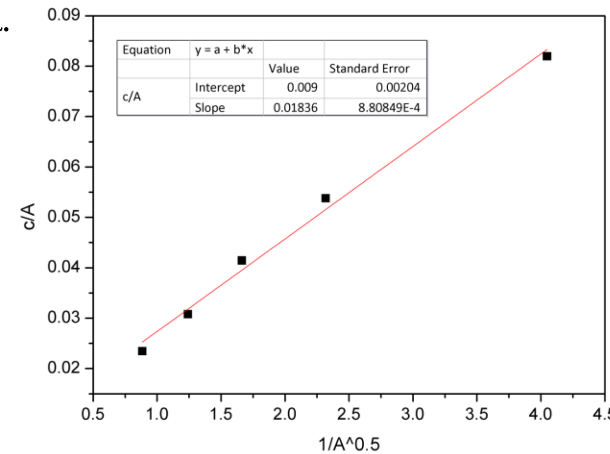
- **Relevance**
  - Rational molecular design has potential to systematically address Li-S cell performance issues, leading to a battery system with 2x energy density compared to Li-ion and high capacity retention
- **Approach**
  - Mesoporous carbon with attached chemical functionality for improved utilization/retention of sulfur
  - IL-based polyelectrolyte gels for Li metal compatibility, reduced polysulfide solubility
  - Polysulfide “trapping” through interaction with designed molecular components to retain and utilize sulfur in cathode
  - Self-healing materials based on NDI/Py to heal mechanical damage from cell operation
- **Technical Progress**
  - High conductivity demonstrated for initial range of freestanding gel electrolyte designs
  - Excellent long-term compatibility of ionogels with Li metal demonstrated
  - Chemical insight into NDI/Py interaction used to develop self-healing polymer system with widely tunable properties
  - Solid-state ion transport and compatibility with IL demonstrated for self-healing materials
  - Mesoporous carbons with thiol functionality developed and characterized as advanced sulfur hosts
  - Functionalized carbon host shown to improve capacity and retention of high-loading sulfur cathodes
- **Future Work**
  - Develop and characterize gel cathodes with improved performance using *in-situ* curing of precursors
  - Select specific material system for continued development with and optimize for cell performance
  - Identify and mitigate degradation pathways in our novel cell designs

Technical Back-Up Slides

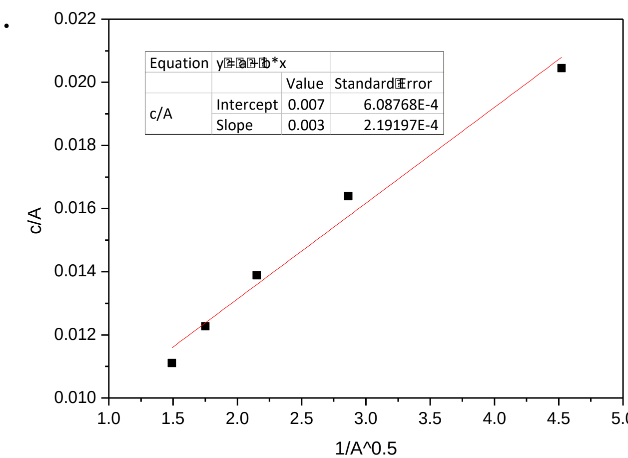
NDI/Py Interaction Modes



a.

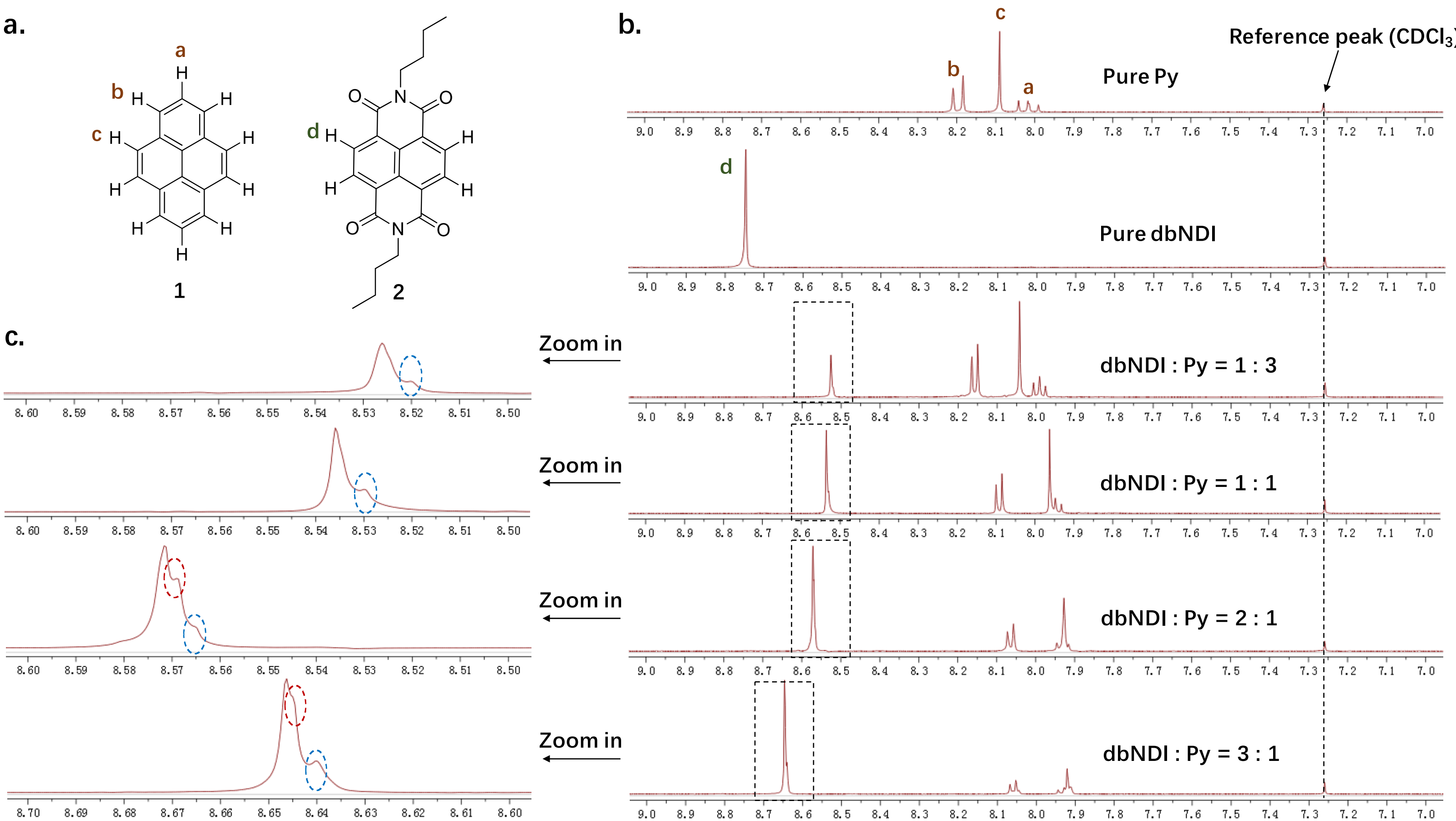


b.



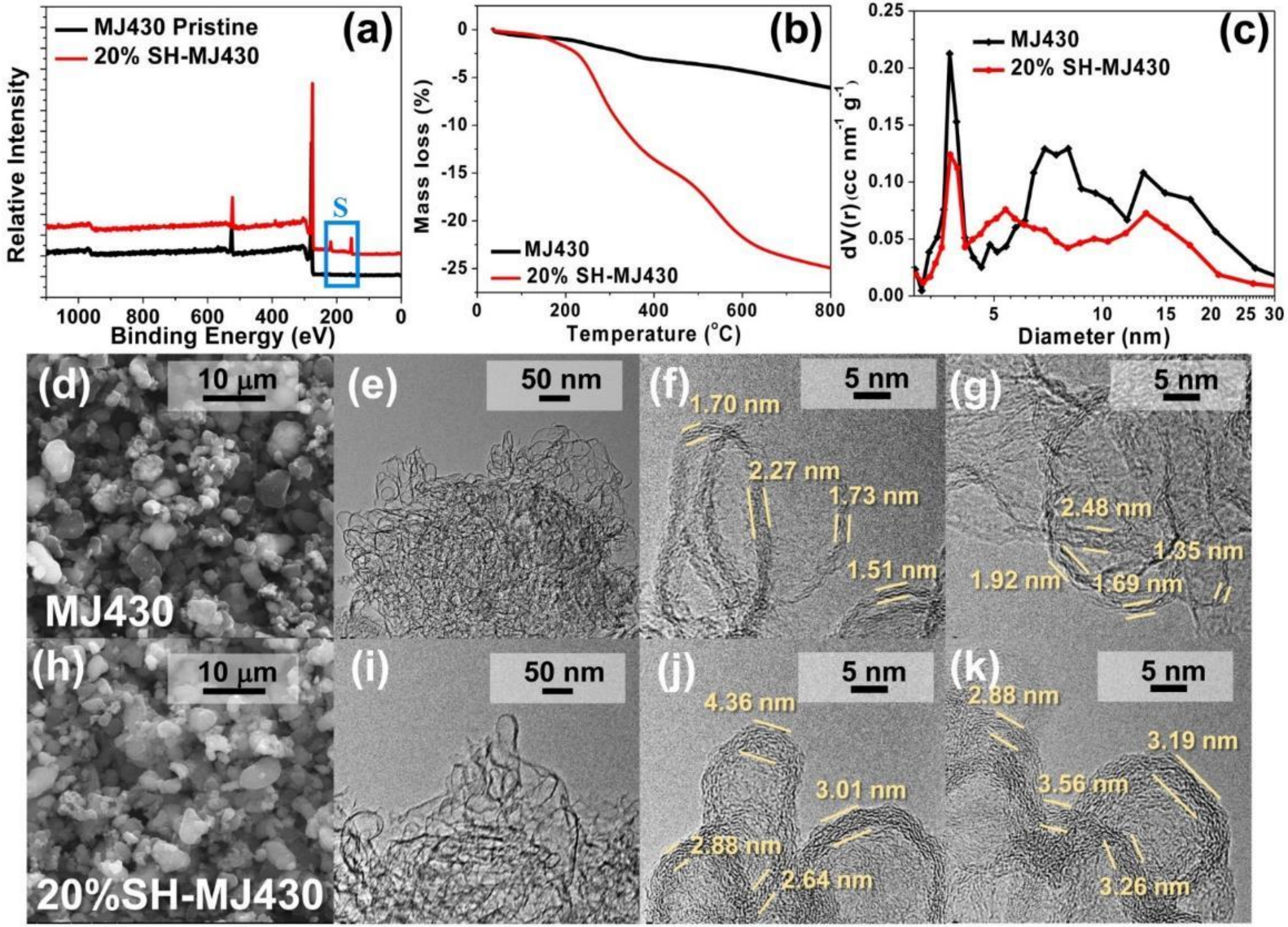
- UV-Vis analysis of dbNDI:Py mixtures indicates two interaction modes
  - 1:1 NDI:Py, 500nm abs, -8.2 kJ/mol,
  - 2:1 NDI:Py, 514nm abs, -16.5 kJ/mol

NDI/Py Interaction Modes



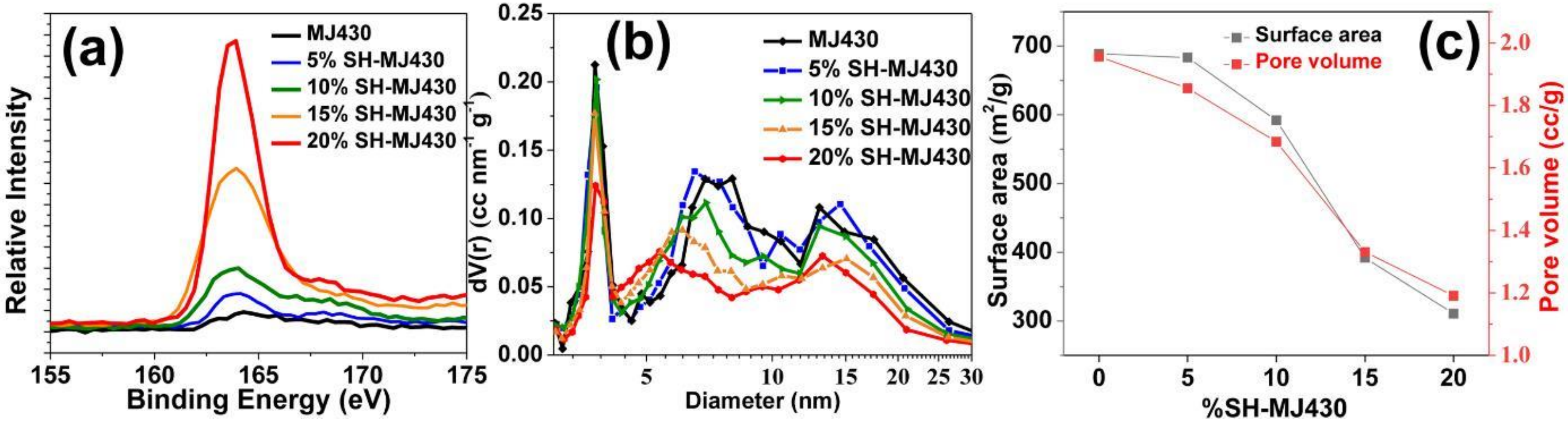
- ^{1}H peak splitting for dbNDI:Py mixtures also indicates concentration-dependent binding

Modified Carbon Characterization



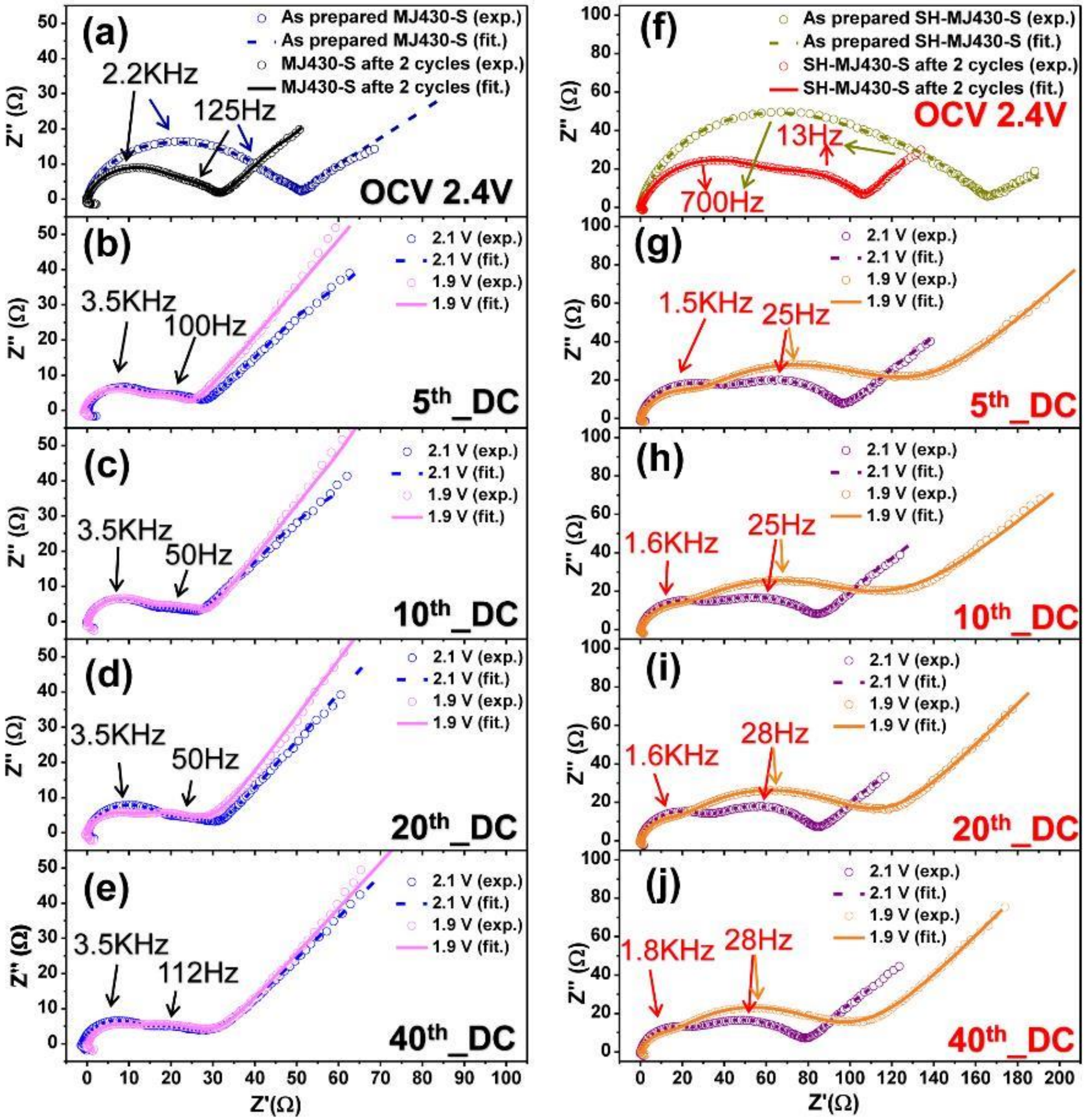
- XPS, TGA, BET isotherms, SEM, and TEM confirm successful thiol functionalization of carbon

Modified Carbon Characterization



- Varying thiol concentration on carbon (measured as %wt loss in TGA relative to baseline) confirmed by XPS and BET isotherms

EIS Analysis of S Cathodes



- Impedance spectra of pristine (left) vs thiol-modified (right) carbon/sulfur cathodes at varying cycle and discharge state
- Larger mid-frequency semicircle in modified samples suggests charge-transfer resistance as origin of increased overpotential